

## SCIENTIFIC COMMUNICATIONS

### DIATREMES ACT AS FLUID CONDUITS FOR Zn-Pb MINERALIZATION IN THE SW IRISH ORE FIELD

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#### Abstract

Irish-type mineralization is commonly attributed to fault-controlled mixing of a seawater-derived, sulfur-rich fluid and basement-derived, metal-rich fluid. However, maar-diatreme volcanoes discovered in close spatial and temporal association with Zn-Pb mineralization at Stonepark in the Limerick basin (southwest Ireland) bring a new dimension to established geologic models and may increase the deposit-scale prospectivity in one of the world's greatest Zn-Pb districts. Stonepark exhibits many incidences of dolomitic black matrix breccias with associated Zn-Pb mineralization, the latter typically occurring within 150 m of the diatremes. Highly negative  $\delta^{34}\text{S}$  pyrite values within country rock-dominated black matrix breccias (–12 to –34‰) are consistent with sulfide precipitation from bacteriogenic sulfur reduction in seawater-derived brines. However,  $\delta^{34}\text{S}$  values of Zn-Pb sulfides replacing black matrix breccias (–10 to 1‰) reflect multiple sulfur sources. Diatreme emplacement both greatly enhanced country rock fracture permeability and produced conduits that are filled with porous volcanoclastic material and extend down to basement rock types. Our  $\delta^{34}\text{S}$  data suggest that diatremes provide more efficient fluid pathways for basement-derived fluids. The diatremes introduce another potential sulfur source and facilitate a greater input of metal-rich basement-derived hydrothermal fluid into the system compared to other Irish-type deposits such as Navan and Lisheen, evidenced by Stonepark's more positive modal  $\delta^{34}\text{S}$  value of –4‰. Irish-type deposits are traditionally thought to form in association with extensional basement faults and are considered unrelated to extensive Carboniferous magmatism. Our results indicate that a direct link exists between diatreme volcanism and Zn-Pb mineralization at Limerick, prompting a reevaluation of the traditional Irish-type ore formation model, in regions where mineralization is spatially associated with volcanic pipes.

#### Introduction

The Irish ore field hosts a number of globally important stratabound, carbonate-hosted Zn-Pb deposits of Viséan age (346.7–330.9 Ma), which exhibit strong spatial and genetic associations with reactivated Caledonian basement faults (Mitchell, 1985; Hitzman and Beaty, 1996; Everett et al., 1999; Hitzman, 1999; Blakeman et al., 2002; Wilkinson et al., 2005a; Ashton et al., 2015; Hnatyshin et al., 2015) and are designated “Irish-type.” Mineralization in the Limerick region is typically hosted in dolomitized country rock breccias termed “black matrix breccias” (Hitzman et al., 2002; Wilkinson et al., 2005b; Redmond, 2010). The exact origin of these deposits remains controversial, as they share characteristics of both sedimentary exhalative (SEDEX; Wilkinson, 2014) and Mississippi Valley-type (MVT) deposits (Bradley and Leach, 2003). The 2010 discovery of base metal mineralization associated with volcanic rocks in southwest Ireland (Redmond, 2010; Blaney et al., 2013) challenged the traditional Irish-type model, which does not recognize a link to volumetrically minor, but regionally extensive, Carboniferous magmatism

that extends across Ireland, Scotland, and the English Midlands (Davies et al., 2000; Holland and Sanders, 2009; Elliott et al., 2015). Field observations at Limerick (Fig. 1) suggest a close spatial and temporal association between Zn-Pb mineralization and basaltic maar-diatreme volcanism (McCusker and Reed, 2013; Elliott et al., 2015), but the existence of a direct genetic link is yet to be established.

Here, we apply  $\delta^{34}\text{S}$  analysis of sulfides from mineralized environments including volcanic facies and black matrix breccias at Stonepark, Limerick, to investigate the relationship between volcanism and ore deposition. Our data indicate that diatreme emplacement strongly influenced mineral deposit formation at Stonepark. Diatremes, such as those preserved at Stonepark (Elliott et al., 2015), are typically infilled with porous and permeable material (e.g., White and Ross, 2011; Afanasyev et al., 2014) and are associated with fracture networks and breccia bodies related to their explosive emplacement (Sparks et al., 2006). We propose that the relatively permeable diatremes served as conduits for mineralizing fluids, forming more efficient fluid pathways from the basement than the extensional fault systems widely observed within the Irish ore field (e.g., Silvermines, Navan, Lisheen). Our data also suggest that large quantities of volcanoclastic material within the diatreme provided a third (magmatic) sulfur source.

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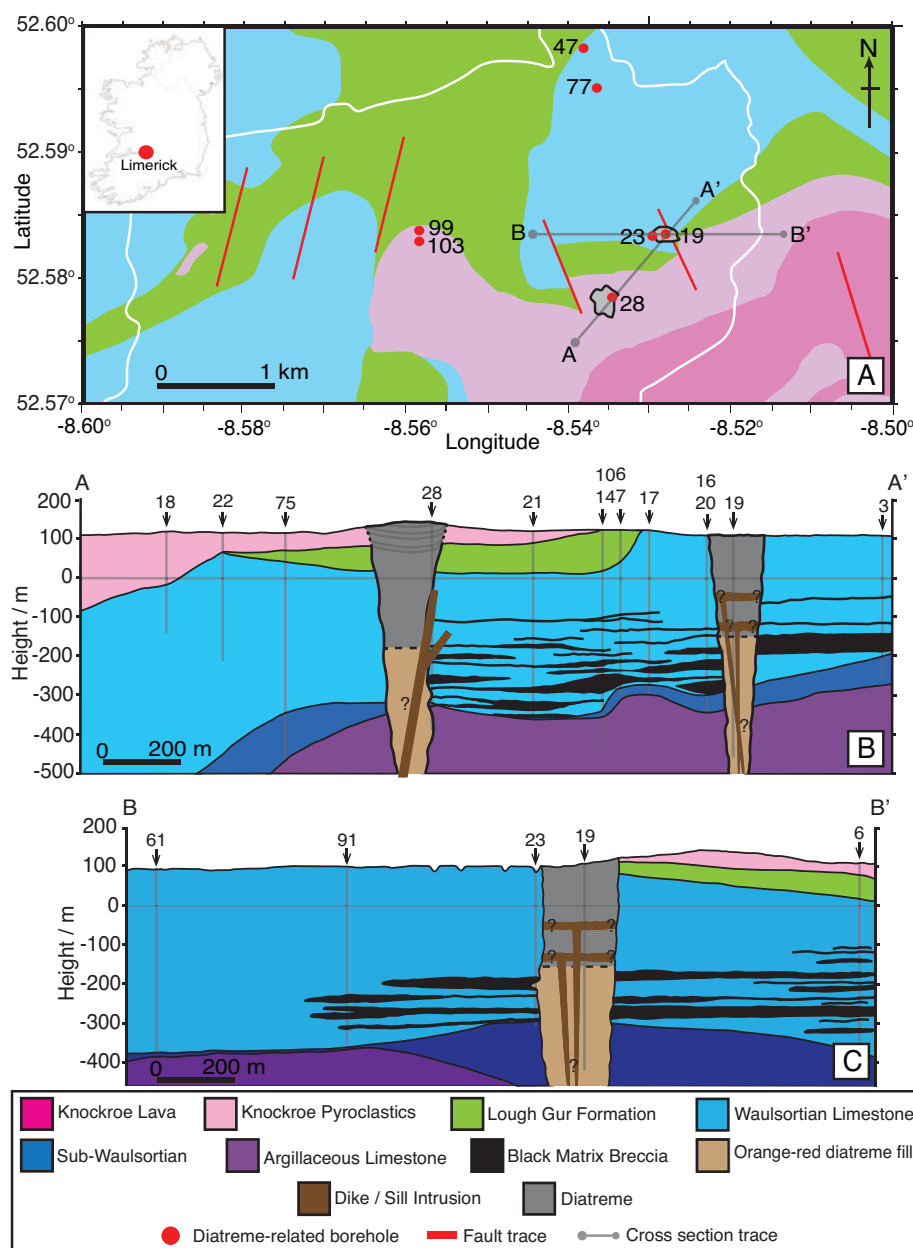


Fig. 1. (A) Summary geologic map of the study area outlined with a white line, showing inferred diatreme outlines (resolved by drill core and magnetic surveys) and boreholes intersecting diatremes. Inset map of Ireland shows the location of Limerick. (B) Southwest to northeast cross section and (C) west to east cross section (see A for locations) showing diatremes and adjacent black matrix breccias. Dotted lines on diatremes indicate upper extent of dolomitization and subsequent hematization overprinting basal parts of diatremes. Y-axis depicts height relative to sea level.

### Context and mineralization

Maar diatremes (hereafter, diatremes) are formed during explosive volcanism (cf. Sparks et al., 2006; White and Ross, 2011). In the Limerick basin, diatremes form a NE-SW-orientated cluster, closely reflecting the regional Caledonian trend. This suggests that ascending magmas utilized preexisting faults (cf. Kurszlaukis and Barnett, 2003; Jelsma et al., 2009). Phreatomagmatic eruption of these diatremes into a shallow-water graben resulted in the deposition of >450 m of extratent pyroclastic deposits (Knockroe Formation) interbedded with wackestones and cherts (Elliott et al., 2015).

Stratigraphic constraints suggest diatreme emplacement occurred during the Viséan stage (346.7–330.9 Ma) (Somerville et al., 1992; Holland and Sanders, 2009).

The Limerick basin occupies a highly faulted section of the western Irish Midlands (Fig. 1). Here, shallow marine carbonates were deposited during the Lower Carboniferous (Holland and Sanders, 2009). Typically, it is the Waulsortian Limestone Formation that hosts high incidences of black matrix breccia. Three main types of black matrix breccia are recognized at Limerick (Fig. 2), all of which have a dolomite-rich matrix ( $\leq 80$  wt %). Country rock black matrix breccia (type C) contains Waulsortian carbonate clasts, commonly

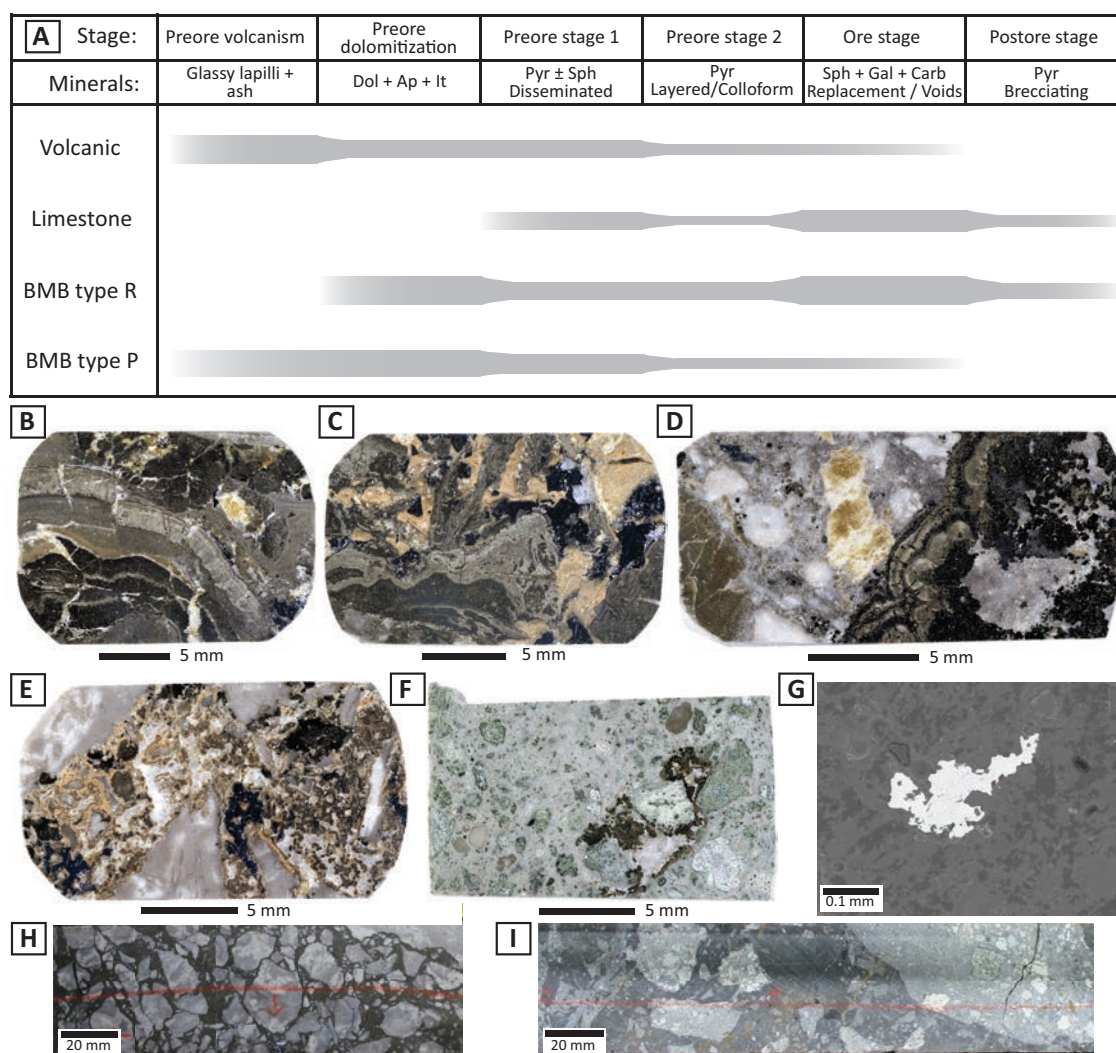


Fig. 2. (A) Summary of the mineralogy and relative importance of each stage of volcanism, dolomitization, and mineralization within the studied categories. (B) Sample 6476; replacement of black matrix breccia (type R) by layered preore stage 2 pyrite and ore-stage minerals brecciated by postore fine-grained pyrite. (C) Sample 6508; replacement of limestone breccia by the same mineral assemblage seen in B. (D) Sample 6470; polymict breccia (type P) replaced by layered and colloform stage 2 pyrite, later replaced by ore-stage spherules of sphalerite. (E) Sample 6500; ore-stage vein of sphalerite, galena, and carbonate crosscutting Waulsortian limestone. (F) Sample 6496; pyrite replaced by sphalerite rimming clasts in diatreme fill. (G) Sample S17; scanning electron microscope image of sphalerite replacing matrix of diatreme clast. (H) Country rock breccias (type C); weakly mineralized with minor pyrite and Waulsortian limestone clasts displaying embayed edges and often jigsaw or float textures (borehole TC-2638-036, 223.1 m below sea level [b.s.l.]). (I) Polymict breccias (type P); diatreme clasts and matrix partially replaced by pyrite (borehole TC-2638-047, 0.6 m b.s.l.). Abbreviations: Ap = apatite, BMB = black matrix breccia, Carb = carbonate, Dol = dolomite, Gal = galena, It = illite, Pyr = pyrite, Sph = sphalerite.

with embayed edges set in a dark, relatively unmineralized matrix that exhibits limited pyrite replacement (Fig. 2A). Replaced black matrix breccia (type R) contains clasts and matrix completely or predominantly replaced by sphalerite, galena, and pyrite (Fig. 2B). Polymict black matrix breccia (type P) contains a range of clast types, including diatreme breccia, pyroclastics, crystalline igneous, and country rock, in a poorly mineralized dolomite matrix (Fig. 2C) intruded by tuffsite dikes. Volcaniclastic material within the breccia occasionally shows evidence of deformation prior to lithification (Elliott, 2015), indicating that these clasts were still unconsolidated when they were incorporated into the breccia.

Mineralized or black matrix breccia clasts have not yet been observed in the diatreme fill, which has been dolomitized and subsequently hematized, causing a red coloration. Dolomitization of the diatreme fill starts at ~100 to 190 m below sea level (m b.s.l.), coinciding with higher incidences of black matrix breccia in the country rock (Fig. 1). Concentrations of dolomite within the upper diatreme fill range from 0.2 to 0.4 wt %, increasing to 11 to 12 wt % in the middle diatreme (110–190 m b.s.l.) and 22 wt % at >400 m b.s.l. Dolomite is a key black matrix breccia mineral phase, constituting ≤80 wt % of the breccia matrix. Further, the lower diatreme fill (>400 m b.s.l.) exhibits the same mineral assemblage as black matrix breccia type P clasts, comprising dolomite,



illite, calcite, and quartz, suggesting they experienced similar hydrothermal alteration (Elliott, 2015). The lower diatreme matrix contains higher concentrations of disseminated sphalerite, pyrite, rutile, and galena than the upper and middle diatreme. These observations strongly suggest that diatreme emplacement predated, or was synchronous with, black matrix breccia formation and that mineralization post-dated both events.

Black matrix breccias are concentrated in fractured country rock adjacent to the diatremes, typically pinching out with distance from the diatreme margins (Fig. 1C). Major and trace element signatures of juvenile volcanic fragments in the type P breccias, diatreme fill, and Knockroe Formation pyroclastic material are geochemically near identical (Elliott et al., 2015).

### *Role of faulting and hydrothermal fluids*

There is some controversy surrounding the relative importance and timing of large-scale extensional basement faults that provided fluid pathways; however, there is a general consensus that the majority of Irish-type deposits were formed by the epigenetic sulfide replacement of hydrothermal breccias (e.g., Hitzman and Beaty, 1996; Anderson et al., 1998; Hitzman et al., 2002; Wilkinson et al., 2005b; Redmond, 2010). The timing of mineralization at Lisheen and Silvermines has been constrained by Hnatyshin et al. (2015) to  $346.6 \pm 3.0$  and  $334.0 \pm 6.1$  Ma, respectively, and within a similar time frame to Stonepark.

Different black matrix breccia types have been recognized in the literature; however, some show evidence for formation by sedimentary processes within cavities, later overprinted by hydrothermal fluids (e.g., Lee and Wilkinson, 2002). However, typical black matrix breccias are thought to have formed by hydrothermal fluids that utilized extensional faults, brecciating the carbonate host rocks (Hitzman and Beaty, 1996; Hitzman et al., 2002). These breccias were later affected by large-scale sulfide precipitation (Wilkinson et al., 2005b) upon mixing of surface- and basement-derived hydrothermal fluids (Banks et al., 2002; Wilkinson et al., 2005a). The surface fluid is thought to be a lower-temperature ( $<140^\circ\text{C}$ ) seawater-derived brine, enriched in reduced bacteriogenic sulfur ( $-25$  to  $-5\%$ , mean  $-15\%$ ; Fallick et al., 2001), which had evaporated to reach salinities of up to 25 wt % NaCl equiv. The second, higher-temperature ( $200$ – $280^\circ\text{C}$ ) hydrothermal fluid likely contained a high concentration of metals and minor reduced hydrothermal sulfur ( $0$ – $15\%$ , mean  $10\%$ ; Fallick et al., 2001), leached from basement rocks (Fallick et al., 2001; Banks et al., 2002).

### *Sulfide description and paragenesis*

Sulfide precipitation at Limerick is multistage, similar to that at other deposits in the Irish ore field (e.g., Hitzman and Beaty, 1996; Hitzman et al., 2002; Ashton et al., 2015). Early fine-grained, disseminated pyrite (preore 1) is observed in all environments but can be associated with rounded aggregates of dark sphalerite within black matrix breccia horizons (Fig. 2D). Another void-filling pyrite mineralization stage follows (preore 2), typically precipitated in layers or with a colloform habit (Fig. 2B, D). Within the diatreme fill, this stage is represented by massive or coarse-grained pyrite locally replacing juvenile ash rimming volcanic clasts or is associated with carbonate-filled voids (Fig. 2F).

The subsequent main ore-forming stage is represented differently in each environment. Unfortunately, sphalerite and galena crystals within the lower diatreme are too small to perform sulfur isotope analysis but have been identified and imaged by scanning electron microscope (SEM) (Fig. 2G). These minerals appear to coprecipitate as anhedral masses predominantly replacing volcanic lapilli or earlier pyrite. Earlier pyrite within black matrix breccia samples is brecciated or replaced by ore minerals at this stage (Fig. 2B, C). Within type R black matrix breccias, galena is typically observed as large anhedral crystals and sphalerite as creamy yellow-brown anhedral intergranular masses, often associated with carbonate filling voids (Fig. 2B). A similar assemblage is observed within the Waulsortian limestone environment, as veins replacing crackle breccias or as sediment infilling voids. Sphalerite is typically found at the edge of veins or rimming clasts in breccias and is occasionally layered, whereas anhedral galena and carbonate fill the voids (Fig. 2C, E). Pure sphalerite veins within the limestone consist of elongate brown crystals. Sphalerite and galena are sparse within type P black matrix breccia samples but can replace the matrix and earlier layered or colloform pyrite (Fig. 2D).

Postore fine-grained veins of pyrite intrude, brecciate, and in some cases replace earlier stages of mineralization (Fig. 2B, C). This is observed in all sampled environments except the volcanic material, in which sphalerite and galena are the latest mineralization stages identified.

### **Analytical Techniques**

Sulfides (pyrite, sphalerite, and galena) from black matrix breccias, sedimentary rocks, intrusions, diatremes, and veins were separated from gangue by crushing and picking or microdrill extraction and analyzed for sulfur isotopes following the approach used by Robinson and Kusakabe (1975). Samples of fine-grained sulfides and those exhibiting intergrown sulfide textures were prepared as polished blocks and combusted by in situ laser analysis (Wagner et al., 2002). The laser spot size was  $\sim 100\ \mu\text{m}$ , significantly smaller than the scale of intergrowths, which typically range from 400 to  $6,000\ \mu\text{m}$ . Reproducibility based on repeat analysis of internal and international standards was  $\sim \pm 0.3\%$  for both methods. All data are reported in  $\delta^{34}\text{S}$  notation as per mil ( $\%$ ) variations from the Vienna Canyon Diablo Troilite (V-CDT).

### **Sulfur Isotope Results**

The Waulsortian Limestone Formation hosts the diatremes and black matrix breccias and contains pyrite-carbonate-filled veins and breccias. Limestone-hosted sulfides (pyrite, sphalerite, and galena; see App. Table A1) consist of preore stage 1, stage 2, and ore-stage minerals that returned predominantly negative  $\delta^{34}\text{S}$  values ( $-45$  to  $-1\%$ ), with a mean of  $-10.9\%$ . Only three samples out of the 16 analyzed show fine-scale inhomogeneity, displaying values up to  $12\%$  (Fig. 3A). Ore-stage sulfides display a more positive mean  $\delta^{34}\text{S}$  value of  $-7.5\%$  compared to preore stages ( $-17$  to  $-14\%$ ).

Type C black matrix breccias contain preore stage pyrite with negative  $\delta^{34}\text{S}$  values ( $-34$  to  $-13\%$ ; Fig. 3B; App. Table A2). In contrast,  $>70\%$  of type R black matrix breccia  $\delta^{34}\text{S}$  values (pyrite, sphalerite, and galena) lie in the range from  $-10$  to  $1\%$  (mode  $-4\%$ ). Preore stage 2 sulfides (mean  $-7\%$ ) and

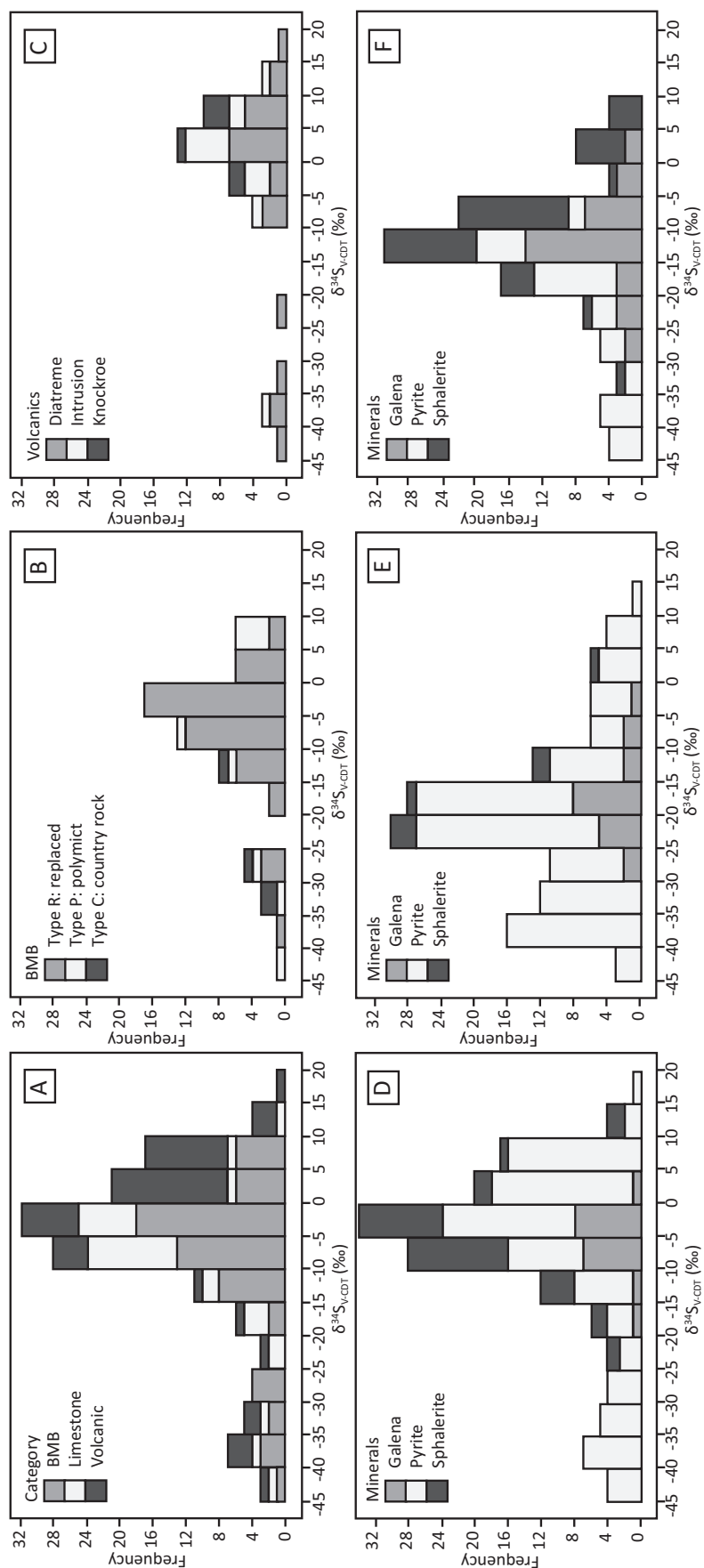


Fig. 3. Histograms of sulfur isotope results (raw data available in App. Table A1). (A) Data categorized by environments: black matrix breccia, limestone, and volcanic rock-hosted sulfides. (B) Black matrix breccia data categorized by type. Type R contain high concentrations of sulfides; type P contain moderate concentrations, predominantly pyrite; and type C are typically unmineralized. (C) Volcanic-hosted sulfide data generalized in Figure 3A is here categorized by host rock (diatreme fill, intrusions, or extracater deposits of the Knockroe Formation). (D) Sulfur isotope results categorized by mineral type from all environments. For comparison, sulfur isotope data from (E) Silvermines (Boyce et al., 2003) and (F) Lisheen (Wilkinson et al., 2005b) are shown categorized by mineral type. Abbreviations: BMB = black matrix breccias, V-CDDT = Vienna-Canyon Diablo Troilite.

ore-stage sulfides (mean  $-5\text{‰}$ ) display similar ranges of  $\delta^{34}\text{S}$  values. However, preore stage 1 sulfides display more negative  $\delta^{34}\text{S}$  values (mean  $-20\text{‰}$ ). Type P black matrix breccias are variably mineralized with pyrite and minor sphalerite and galena, reflected in the wide distribution of  $\delta^{34}\text{S}$  values ( $-44$  to  $10\text{‰}$ ; Fig. 3B; App. Table A2). Compared to the other black matrix breccia environments, type P ore-stage sulfides exhibit more positive  $\delta^{34}\text{S}$  values (mean  $6\text{‰}$ ).

Sulfides (predominantly pyrite) from volcanic rocks exhibit a more restricted range of  $\delta^{34}\text{S}$  values, largely between  $-10$  and  $10\text{‰}$  (Fig. 3C). Due to their disseminated nature in the diatreme fill, ore-stage sulfides were only able to be sampled from intrusions and displayed a mean  $\delta^{34}\text{S}$  value of  $5.5\text{‰}$ . Preore stage 1 sulfide minerals within diatreme and intrusion samples exhibit more negative  $\delta^{34}\text{S}$  values (mean  $-4$  and  $-7\text{‰}$ , respectively) than those from preore stage 2, which typically show more positive  $\delta^{34}\text{S}$  values (mean  $2$  and  $3\text{‰}$ , respectively).

#### *Comparison with other deposits in the Irish ore field*

Sulfides at Silvermines show a bimodal  $\delta^{34}\text{S}$  distribution with modes at  $-21$  and  $-36\text{‰}$  (Fig. 3E). In contrast, minerals from Lisheen show a unimodal  $\delta^{34}\text{S}$  distribution with a mode of  $-10\text{‰}$  (Fig. 3F). Our data from Stonepark (Fig. 3D) have a distinctly more positive distribution compared to the other two deposits, with a mode of  $-4\text{‰}$  (App. Table A2). A highly negative pyrite peak is common to all deposits, visible between  $-40$  to  $-35\text{‰}$  (Fig. 3).

Sulfides adjacent to faults at Navan and Lisheen typically exhibit more positive  $\delta^{34}\text{S}$  values (Blakeman et al., 2002; Wilkinson et al., 2005b), suggesting they accommodated basement-derived fluids (Blakeman et al., 2002; Wilkinson et al., 2005b). To some extent this relationship is observed at Limerick, where positive  $\delta^{34}\text{S}$  values of sphalerite and galena are solely observed proximal to the diatremes ( $<116$  m). However, negative  $\delta^{34}\text{S}$  values of these sulfides are observed at all distances from the diatremes, up to  $410$  m (Fig. 1B, C).

Sulfur isotope data for the adjacent Pallas Green deposit (currently owned by Glencore PLC) are sparse, but those available indicate a similarly positive value ( $\sim 10\text{‰}$ ; Wilkinson and Redmond, 2010). A number of volcanic centers have also been identified at Pallas Green, in addition to many dikes, sills, and intrusive breccia plugs (Tyler, 2007), with the latter likely diatremes. Tyler (2007) also describes breccia dikes containing  $<30\%$  igneous clasts, comparable with type P black matrix breccias described herein, which are often associated with ore-grade mineralization.

### **Discussion and Conclusions**

Grades of Zn and Pb mineralization are high within black matrix breccia horizons proximal to the diatremes ( $\leq 27$  wt %; see App. Table A3) and reduce significantly with distance from the diatreme margins (Fig. 4). This pattern supports the hypothesis that basement-derived, metal-rich fluids preferentially utilized the diatremes. Anomalously high Zn concentrations ( $>20$  wt %) occur at shallower depths adjacent to diatremes in the northwest (Fig. 4C), compared to the southeast (Fig. 4D). Lead concentrations show a similar pattern, displaying  $<30$  wt % at shallower depths surrounding the northern diatreme-related boreholes (Fig. 4A); however,

comparable concentrations to the south are observed at  $350$  m (Fig. 4B). This could be related to the thick composite intrusions observed within diatreme 19 (Fig. 1B, C) acting as a barrier and focusing fluids into the surrounding country rock at greater depths to the southwest.

Negative  $\delta^{34}\text{S}$  values within type C black matrix breccias are consistent with a bacteriogenic sulfur origin, most likely precipitated from seawater-derived brines. The light sulfur isotopes and lack of ore-stage minerals support the hypothesis that metal-rich, basement-derived fluids never reached these breccias. In contrast, type R black matrix breccias show evidence for a shift to more positive values, which could be explained by mixing of two fluids, resulting in extensive sulfide precipitation (Fig. 5B). Early preore stage 1 sulfides display highly negative  $\delta^{34}\text{S}$  values, indicating they precipitated from seawater-derived brines. The introduction of metal-rich, basement-derived fluids containing heavier sulfur isotopes resulted in more positive isotopic signatures in the later preore stage 2 and ore-stage sulfides.

Type P black matrix breccia sulfides exhibit the widest range of  $\delta^{34}\text{S}$  values, consistent with bacteriogenic sulfate reduction ( $-45\text{‰}$ ) and more positive sulfur leached from basement rocks ( $10\text{‰}$ ). Heavier sulfur isotopes may also have been leached from the large volumes of diatreme-, intrusion-, and Knockree-related material hosted in these breccias, with means between  $-2.1$  and  $3.8\text{‰}$  (see App. Table A2). Country rock-hosted sulfides exhibit predominantly negative  $\delta^{34}\text{S}$  values (see Fig. 3A). These data suggest that seawater-derived fluids utilized both fractured country rock and diatreme pathways, whereas basement-derived fluids were restricted to the diatremes and subsequently formed type P black matrix breccias (Fig. 5B). Fluid mixing in type R breccias led to extensive sulfide precipitation.

It is well established that diatreme-filling deposits have high initial porosity and permeability (Sparks et al., 2006; Stripp et al., 2006), allowing enhanced hydrothermal fluid flow (Afanasyev et al., 2014). Further, diatreme-forming eruptions produced radial fracture networks (cf. Barnett and Lorig, 2007), allowing fluid flow in and out of the diatremes. The localization of black matrix breccias adjacent to and radiating out from the diatreme margins (Fig. 1B, C) most likely reflects exploitation by fluids of fracture networks associated with diatreme emplacement. High Zn and Pb grades ( $<22$  and  $7.5$  wt %, respectively) are also observed  $<50$  m from the diatremes and reduce significantly with distance from the diatreme margins (Fig. 4).

Hydrothermal components increase in importance during the later stages of Irish-type ore formation (e.g., Lisheen; Wilkinson et al., 2005b). The Stonepark deposit exhibits a more positive sulfur isotope signature in later sulfide precipitation stages compared to other Irish ore field deposits. We attribute this to enhanced hydrothermal fluid flux from the basement, via 1- to 2-km-deep diatremes, which would increase the amount of hydrothermal sulfur relative to bacteriogenic sulfur in the mineralizing system. In summary, the evidence for enhanced fluid flow from the basement via diatremes is as follows: (1) dolomite, a key black matrix breccia mineral, overprinting the lower diatreme fill, (2) the occurrence of mineralization within the lower diatremes, (3) high Zn-Pb mineralization grades proximal to diatreme margins

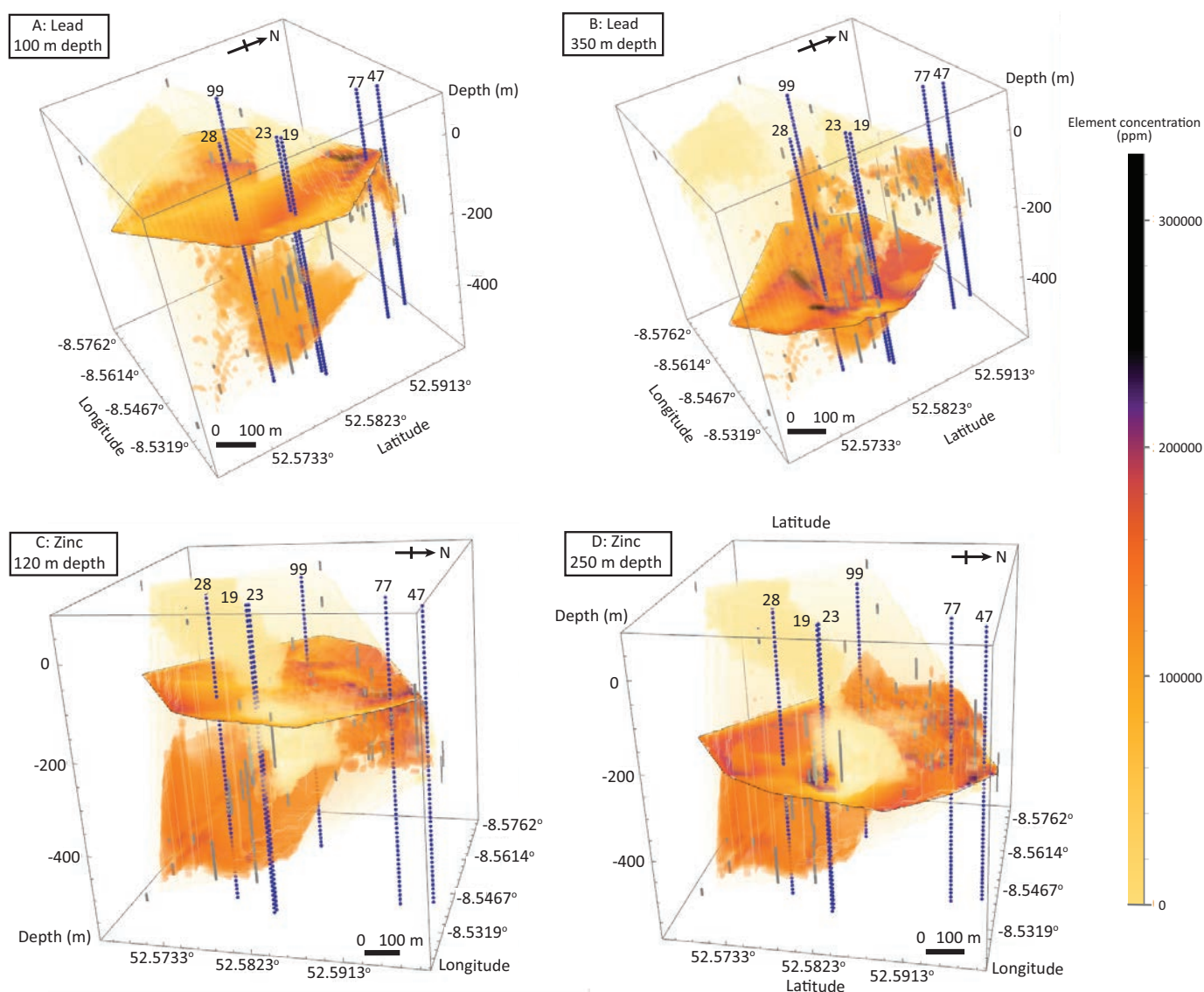


Fig. 4. 3-D box models displaying variations in concentration of lead and zinc (ppm), showing plan sections through the model at varying depths within the northeast section of the Limerick license area. Gray lines show depths within boreholes where assay Zn and Pb concentrations have been measured (see App. Table A3). The model was created by extrapolating these values in all directions. Dotted blue lines show traces of diatreme-related boreholes identified by the number above, and depth is recorded as meters below sea level (m b.s.l.). 3-D box models display lead concentrations with plan sections at 100 m b.s.l. (A) and 350 m b.s.l. (B) in addition to zinc concentrations with plan sections at 120 m b.s.l. (C) and 250 m b.s.l. (D).

(Fig. 4), and (4) the more positive sulfur isotope signatures observed in the Stonepark deposit (Fig. 3C). The latter is enhanced by the leaching of a third magmatic sulfur source (mean  $-0.4\text{‰}$ ; see “Intrusion (original)” in App. Table A1) from basaltic glass-rich pyroclastic diatreme fill (estimated minimum volume for a given vent  $\sim 5\text{--}7.5 \times 10^6 \text{ m}^3$ ; Elliott et al., 2015) during hydrothermal alteration (cf. Afansyev et al., 2014).

The timing of mineralization in the Irish ore field (Chadian to Arundian; Hitzman and Beaty, 1996; Anderson et al., 1998; Reed and Wallace, 2004; Ashton et al., 2015) overlaps with extensive magmatic and volcanic activity, including that in the Limerick basin (Somerville et al., 1992; Elliott et al., 2015; Hnatyshin et al., 2015; Wilkinson and Hitzman, 2015). Textures

such as plastic deformation of diatreme-derived material within black matrix breccia type P indicates that black matrix breccia formation occurred during the waning stages of diatreme activity. Therefore, a close temporal association between volcanism, hydrothermal activity, and mineralization exists at Stonepark and raises the interesting possibility that volcanism is a key process in the localization of Zn-Pb mineralization. The temporal associations at Limerick are consistent with a scenario in which magmatism elevated heat flow and hydrothermal circulation in the Carboniferous Irish ore field (Praeg, 2004; Wilson et al., 2004; Davidheiser-Kroll et al., 2014; Hnatyshin et al., 2015; Wilkinson and Hitzman, 2015).

This study has implications for the origin of diatreme-related mineralization in other regions—for example, in



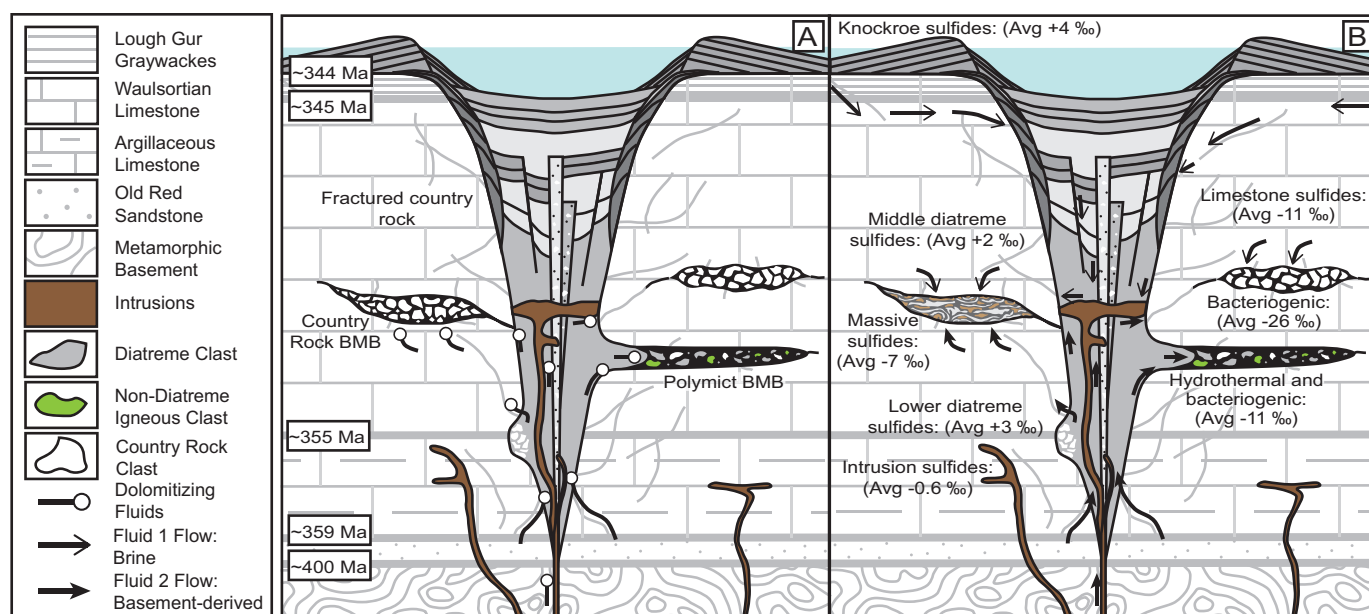


Fig. 5. Schematic summary of the relationship between diatremes, fluid flow, and black matrix breccias (BMBs). (A) Late-stage magmatic intrusions within the diatremes and country rock. Hydrothermal fluids utilize the diatremes, causing dolomitization during the waning stages of eruption. Fluids were channelled into the fractured country rocks, forming dissolution black matrix breccias. (B) Hydrothermal metal-rich and brine-derived hydrothermal fluids utilized the porous diatreme fill. Note  $\delta^{34}\text{S}$  values shown are averages for each category.

gold deposits such as those of Kelian, Indonesia, and Cripple Creek, United States (Davies et al., 2008). Our results suggest that diatreme breccias can focus metal-rich hydrothermal fluids, facilitating epithermal metal deposit formation. The direct link between volcanic activity and Zn-Pb mineralization at Limerick prompts reevaluation of the traditional Irish-type model for ore formation in regions where mineralization is spatially associated with magmatism and volcanic pipes.

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